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Parrish

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(54) **HIGH TEMPERATURE DECOMPOSITION OF HYDROGEN PEROXIDE**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 273 days.

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(22) Filed: **Dec. 6, 2001**

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(51) **Int. Cl.**[7] **C01B 21/36**

(52) **U.S. Cl.** **423/400**; 423/235; 423/239.1; 423/402

(58) **Field of Search** 423/400, 402, 423/235, 239.1

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(57) **ABSTRACT**

Nitric oxide (NO) is oxidized into nitrogen dioxide (NO_2) by the high temperature decomposition of a hydrogen peroxide solution to produce the oxidative free radicals, hydroxyl and hydroperoxyl. The hydrogen peroxide solution is impinged upon a heated surface in a stream of nitric oxide where it decomposes to produce the oxidative free radicals. Because the decomposition of the hydrogen peroxide solution occurs within the stream of the nitric oxide, rapid gas-phase oxidation of nitric oxide into nitrogen dioxide occurs.

11 Claims, 2 Drawing Sheets

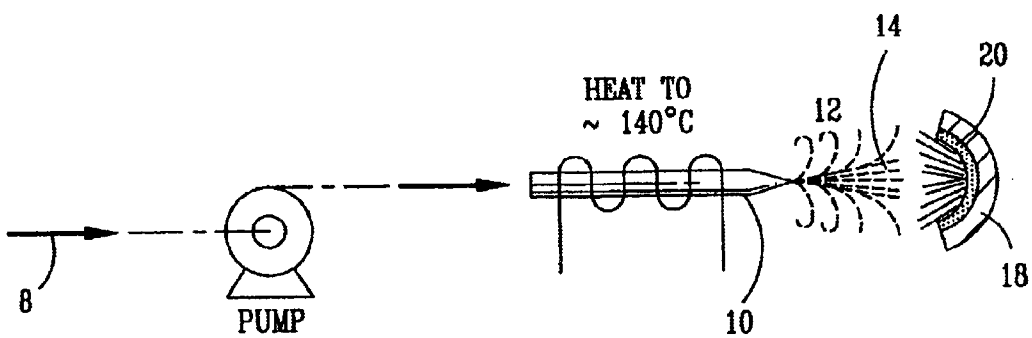


FIG. 1

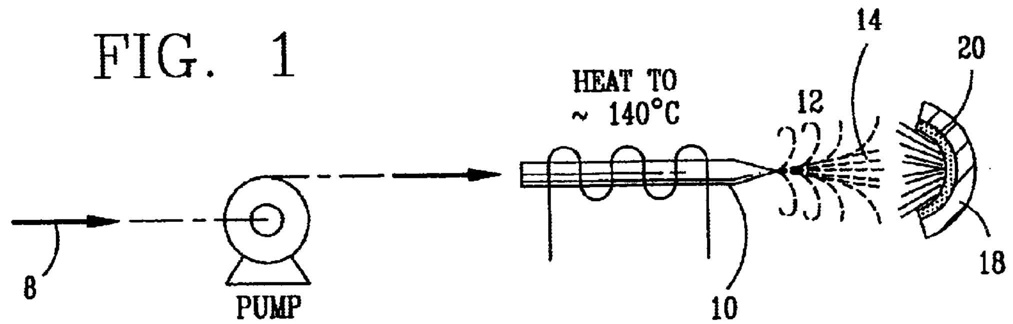


FIG. 3

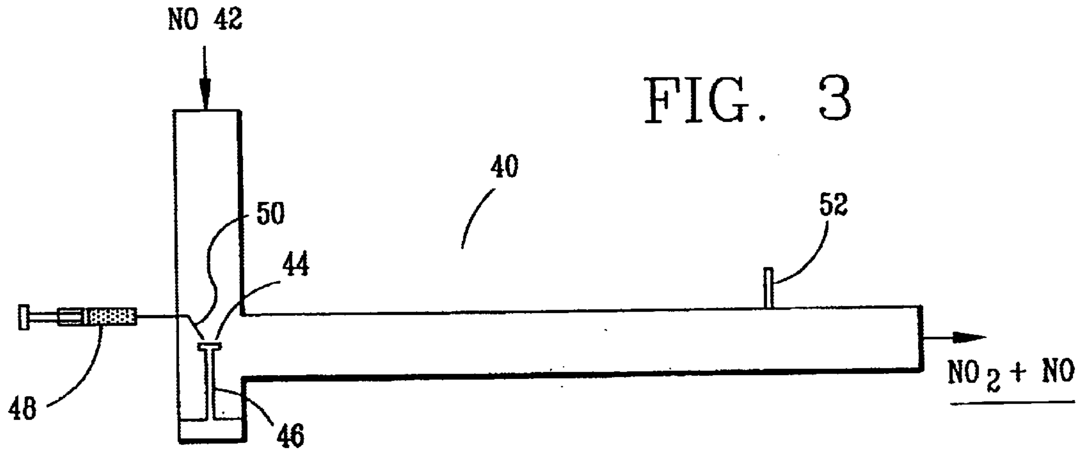
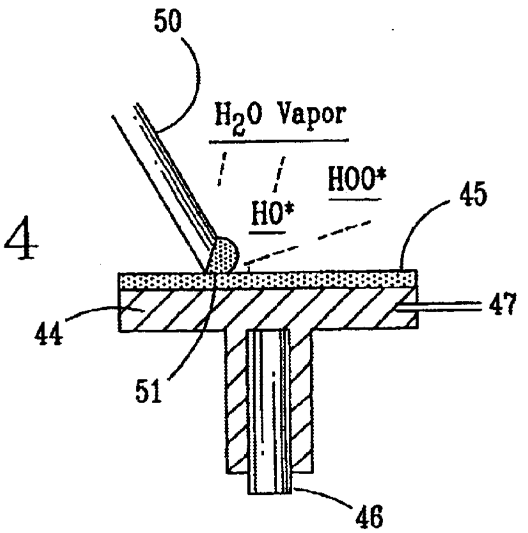


FIG. 4



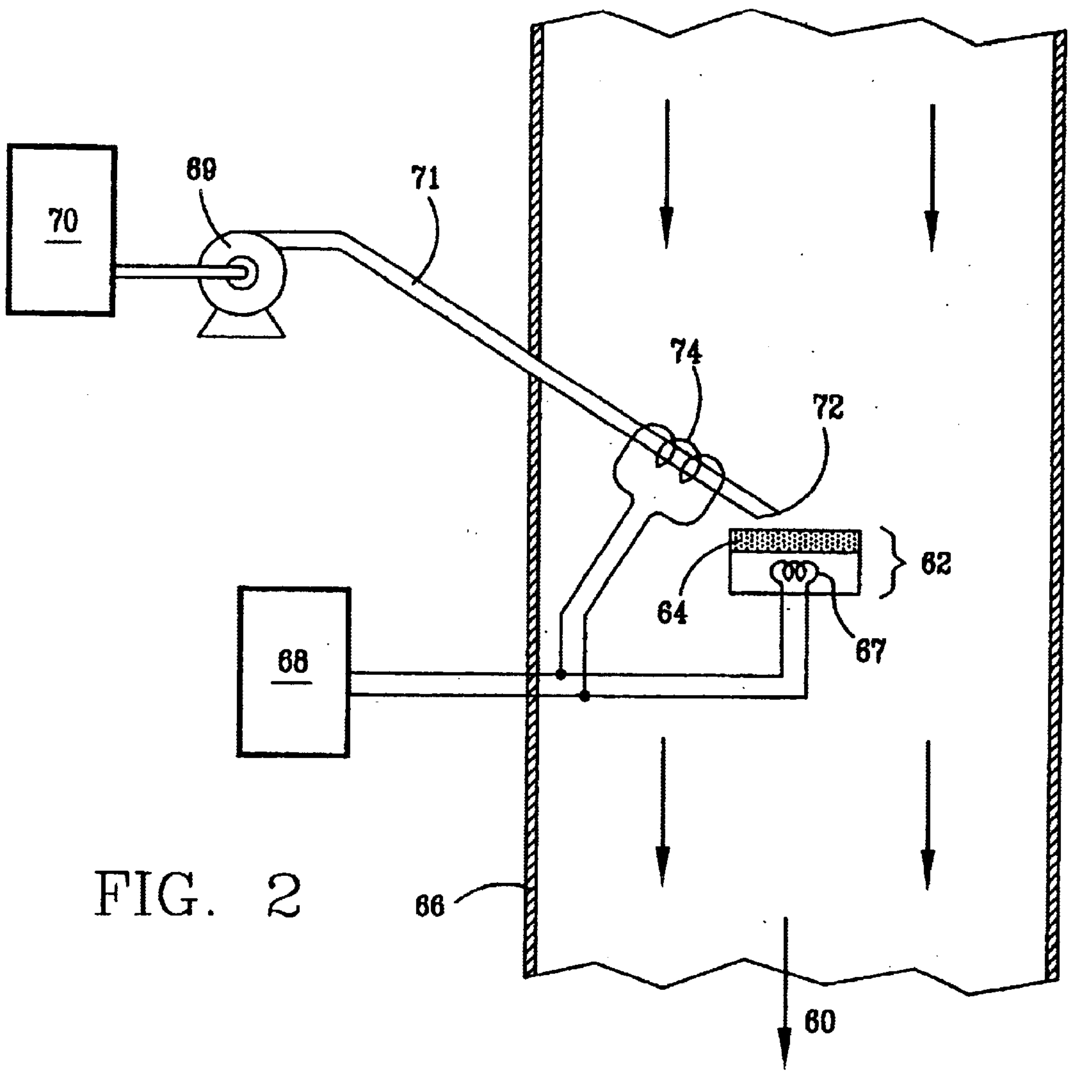

70
69
71
74
72
62
64
67
68
66
60

FIG. 2

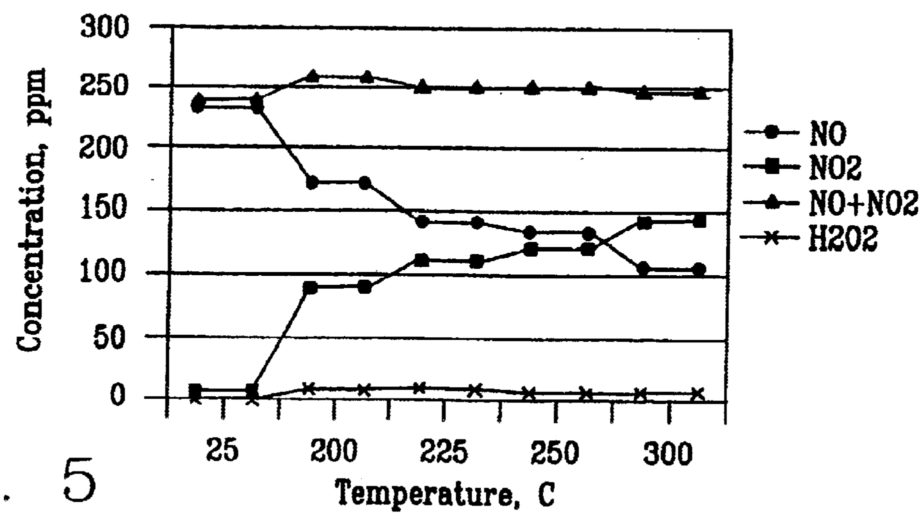

300
250
200
150
100
50
0
Concentration, ppm
NO
NO2
NO+NO2
H2O2
25
200
225
250
300
Temperature, C

FIG. 5

HIGH TEMPERATURE DECOMPOSITION OF HYDROGEN PEROXIDE

PRIORITY CLAIM UNDER 35 U.S.C. § 119(e)

This application claims priority, under 35 U.S.C. § 119(e), on U.S. Provisional Application No. 60/276,260, filed Mar. 8, 2001.

ORIGIN OF THE INVENTION

The invention described herein was made by an employee of the United States Government and may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates generally to a method and apparatus for the high temperature decomposition of hydrogen peroxide to form oxidative free radicals, such as, hydroxyl radical (HO.) and hydroperoxyl radical (HOO.), which oxidize nitric oxide (NO) to nitrogen dioxide (NO_2).

2. Description of the Background Art

Power plants produce a large amount of nitric oxide that must be removed from exhaust gas streams before the gas stream may be emitted into the environment. Effective removal of nitric oxide from the gas stream is complicated by its low water solubility. Although water scrubber systems may be used to aid in the removal of nitric oxide from the gas streams, the effectiveness of the water scrubber system may be increased by oxidizing the nitric oxide to nitrogen dioxide. Nitrogen dioxide is more water soluble than nitric oxide and can be easily removed from the gas streams using various removal processes, such as the water scrubber systems. Although nitric oxide does slowly oxidize in air to nitrogen dioxide, an effective oxidizing agent is needed to make the oxidation of nitric oxide effective at low concentrations (~50 to 350 ppm). This low concentration of NO represents a target planned by the US EPA for power plant applications. By 2004, the EPA will require that coal and oil fired power plants install new controls that lower the NOx emissions to 110 ppm. The 2004 requirement for natural gas NOx emissions will be lowered in 2004 to 50 ppm. Currently, the Selective Catalytic Reduction (SCR) method is the only technology that can meet these 2004 EPA requirements.

Gas-phase oxidation of nitric oxide to nitrogen dioxide may be increased by using ozone, hydrogen peroxide, atomic oxygen, hydroxyl radicals or hydroperoxyl radicals as oxidizing agents. The problems with these materials are their high cost and complexity. Injection of hydrogen peroxide in a heated (300 to 400° C.) nitric oxide gas stream or the introduction of an ultraviolet light source to decompose hydrogen peroxide to form oxidative free radicals are examples of known technology with high processing costs. Another expensive material that has been used to oxidize nitric oxide is ozone. A need therefore exists for a highly effective and low cost method for oxidation of nitric oxide.

SUMMARY OF THE INVENTION

To overcome the foregoing problems, the subject invention provides a method and apparatus wherein a hydrogen

peroxide solution is directed onto a heated surface in a nitric oxide stream so that the hydrogen peroxide is decomposed to form oxidative free radicals, hydroxyl and hydroperoxyl, for the oxidation of the nitric oxide. The hydrogen peroxide solution is preferably delivered to the heated surface through a nozzle, which may also be heated, to increase the concentration of and thereby enrich the hydrogen peroxide solution. Impinging the enriched hydrogen peroxide solution onto a heated surface accelerates the decomposition of hydrogen peroxide. Because the rapid decomposition of hydrogen peroxide occurs on the heated surface, there is no increased risk of explosion of stored hydrogen peroxide solution. Since the high temperature decomposition of hydrogen peroxide to oxidative free radicals, hydroxyl and hydroperoxyl, occurs in a stream of nitric oxide, distribution of the oxidative free radicals in the stream will cause rapid gas-phase oxidation of the nitric oxide to nitrogen dioxide.

This high temperature decomposition process provides a simple way for increasing the instability of hydrogen peroxide to the point of decomposition. The process only requires a small pump, a nozzle, a heated surface, and an optional heated tube. There is no need to heat the gas stream that contains the nitric oxide or to introduce an ultraviolet light source or ozone generator.

This process may be used in small scrubbers or large scrubbers similar to those found in power plants. The basic unit is the same for both applications, but the power plant would use multiple units distributed across the flue stack. The commercial potential for this high temperature decomposition process when used in combination with a wet scrubber for nitrogen dioxide is very large. Power plant applications that control NOx emission are estimated to cost in the billions of dollars. This process is the key to making current technology effective in controlling low-level emissions of nitric oxide found in power plants worldwide.

BRIEF DESCRIPTION OF THE DRAWINGS

The features and advantages of the present invention will become apparent from the following detailed description of preferred embodiments thereof taken in conjunction with the accompanying drawings, in which:

FIG. **1** illustrates an example of the high temperature decomposition process of the subject invention for hydrogen peroxide;

FIG. **2** illustrates an embodiment of the present invention for adding hydrogen peroxide to a nitric oxide exhaust gas stream in a power plant;

FIG. **3** illustrates a laboratory scale apparatus for adding H_2O_2 to a nitric oxide gaseous stream;

FIG. **4** illustrates a heated surface having a catalytic coating that is employed in the apparatus of FIG. **3** for injecting and decomposing hydrogen peroxide; and

FIG. **5** is a graph of Fourier Transform Infrared (FTIR) results of a laboratory scale version of the high temperature decomposition process showing the conversion of nitric oxide to nitric dioxide as measured at the heated surface at temperatures of 25, 200, 225, 250 and 300° C.

DETAILED DESCRIPTION OF TIE PREFERRED EMBODIMENTS

In the preferred embodiments of the present invention, high temperature decomposition of hydrogen peroxide to

form the oxidative free radicals, hydroxyl and hydroperoxyl provides a convenient source of highly effective oxidizing agents for the oxidation of nitric oxide in the gas-phase. This high temperature decomposition process avoids problems of complexity and costs common to other methods for the decomposition of hydrogen peroxide.

An example of the high temperature decomposition process is illustrated in FIG. **1**. Prior to impinging a hydrogen peroxide solution **8** (containing hydrogen peroxide and water) onto a heated surface **18**, the hydrogen peroxide solution **8** may be optionally heated to vaporize some of the water into steam **12**. The hydrogen peroxide solution **8** may be pumped through a tube or nozzle **10**. In this example, the hydrogen peroxide solution **8** is heated to ~140° C. If the hydrogen peroxide solution is heated, water in the heated hydrogen peroxide solution **8** evaporates in the form of steam **12** resulting in an enriched hydrogen peroxide solution **14**. This enriched hydrogen peroxide solution **14** impinges on the heated surface **18** (preferably heated to 200°–500° C.) where oxidative free radicals, hydroxyl and hydroperoxyl, are produced. The decomposition of hydrogen peroxide occurring on the heated surface **18** results in rapid decomposition without increasing the risk of an explosion of the hydrogen peroxide solution **8** that is in storage prior to use. Preferably, the heated surface **18** contains a catalytic coating **20** composed of a variety of compounds including, but not limited to, Fe(II), Fe(III) Cr(II), Cu(II), Pt black, Ag, or Pd. Additionally, the decomposition of hydrogen peroxide may occur on a variety of catalytic coatings **20** including oxide surfaces, such as metal oxides, glass, quartz, Mo glass, Fe_3—xMn_xO_4 spinels, Fe_2O_3 with Cu ferrite, MgO and Al_2O_3. The key element for the high temperature decomposition of hydrogen peroxide is contact with a heated surface **18**, regardless of whether the surface has a catalytic coating **20** or not. Table 1 discloses a number of catalytic coatings **20** and the corresponding heated surface temperatures for decomposing hydrogen peroxide. Presently, iron oxide has given the highest degree of conversion.

TABLE 1

Catalysts and Conditions Used to Decompose Hydrogen Peroxide

Catalyst	Conditions
Silver Oxide	250–507° C.
Iron Oxide	200–415° C.
Ruthenium Oxide	300–491° C.
Silver	244–325° C.

The oxidative free radicals are distributed throughout a gaseous nitric oxide stream, preferably containing 50–350 ppm nitric oxide, to rapidly oxidize NO to NO_2. Once the NO is oxidized to NO_2, it is more water-soluble and can be scrubbed with a wet scrubber system. The heated tube or nozzle **10** and the heated surface **18** could be fabricated as a single unit that is connected to a pump manifold that supplies the hydrogen peroxide and electrical lines that supply the power for electric heaters for the nozzle **10** and heated surface **18**.

The high temperature decomposition process is based on the thermodynamic instability of hydrogen peroxide. High concentrations (over 50%) of hydrogen peroxide in solution are unstable and the rate of decomposition increases by a factor of 2.3 for each 10° C. temperature rise. Therefore, a solution containing hydrogen peroxide and water is used in this high temperature decomposition. Preferably, high temperature decomposition may be used to decompose hydrogen peroxide solutions up to and including 50% by weight or volume. However, the hydrogen peroxide solutions do not have to be pre-concentrated.

As illustrated in FIG. **2**, the high temperature decomposition process is preferably used in an exhaust gas stream **60** of a power plant in order to control nitric oxide emissions. A heated block **62**, which is optionally covered with a catalytic coating **64**, is disposed within an exhaust pipe **66** containing the exhaust gas stream **60**. The block **62** could also be replaced by any other suitable structure having a major surface thereon that can readily be heated. A first heater **67**, which is powered by a power supply **68**, is provided in or adjacent to the block **62** for heating the block **62** to a desired decomposition temperature, preferably 200°–500° C. A pump **69** supplies hydrogen peroxide solution from a storage tank **70** to the heated block **62** via a supply tube **71** terminating with an injection nozzle **72**. An optional, second heater **74**, which is also powered by the power supply **68**, may be attached to the injection nozzle **72** to increase the temperature and concentration of the hydrogen peroxide solution. In order to oxidize nitric oxide in the exhaust gas stream **60**, the hydrogen peroxide solution in the storage tank **70** is injected onto the heated block **62** through injection nozzle **72**, thus forming oxidative free radicals. These free radicals oxidize NO to NO_2, which can be scrubbed with a water solution of hydrogen peroxide. Excess unreacted hydrogen peroxide will be captured by the scrubber and form part of the total requirement for hydrogen peroxide.

Typical gas-phase reactions that occur when hydrogen peroxide is catalytically decomposed are shown below:

$$H_2O_2 \rightarrow 2HO. \quad (1)$$

$$HO.+H_2O_2 \rightarrow H_2O+HOO. \quad (2)$$

$$HOO.+NO \rightarrow NO_2+HO. \quad (3)$$

$$2HO.+H_2O_2 \quad (4)$$

Reactions (2) and (3) represent a chain reaction, which means that once the hydroxyl radical (HO.) forms in reaction (1), reactions (2) and (3) will repeat many times until they are terminated by some impurity or recombination reaction (4). Therefore, reaction (1), the initial decomposition of hydrogen peroxide, only needs to occur for a small percent of the hydrogen peroxide for a large conversion of NO to NO_2 to occur.

EXAMPLE 1

A laboratory scale breadboard version of the subject high temperature decomposition process was used to confirm the conversion of NO to NO_2 when exposed to oxidative free radicals generated from the decomposition of hydrogen peroxide on a heated surface having a catalytic coating. In this example, a compressed gas cylinder that contained 5000-ppm nitric oxide in nitrogen was connected to a flow controller adjusted to provide 0.2 liters per minute of the mixture. The output of the flow controller was mixed with

the output from a second flow controller that provided 4.8 liters per minute of nitrogen. The resulting mixture, which had a concentration of 200 ppm of NO was introduced into a test fixture **40** as illustrated in FIGS. **3** and **4**. The test fixture **40** was fabricated from 2-inch clear PVC tubing that directed the test gas mixture **42** of 200 ppm NO over a mild steel block **44** with a 0.44 square-inch surface area that had an oxidized catalytic coating **45** (iron oxide) or a small stainless steel cup that contained catalytic material. A cartridge heater **46** connected to a variable-voltage transformer (not shown) was inserted into the steel block **44**. In addition, a thermocouple **47** was inserted into the steel block **44** to measure the surface temperature. A syringe pump **48** was used to provide a controlled flow of 40-volume percent hydrogen peroxide solution **51**, which was delivered at a rate of 1 to 3 milliliter (mL) per hour to a syringe needle **50** that touched the heated steel block **44**. The syringe needle **50** was configured so the heated steel block **44** also heated the needle tip, which helped increase the concentration of the hydrogen peroxide solution **51** as it contacted the surface of the heated steel block **44**. The conversion of NO to NO_2 was measured at sample point **52** by ASTM Method D-1607 and a Fourier Transform Infrared (FTIR) method developed for this application.

The FTIR results are summarized in the graph of FIG. **5**, where the concentrations of NO, NO_2, NO plus NO_2, and hydrogen peroxide are plotted versus the temperature of the heated surface or steel block **44**. It can be seen from the data illustrated in FIG. **5** that the concentration of NO decreases as the concentration of NO_2 increases, while the sum of the concentrations remains constant. This constant sum indicates that there is direct conversion of NO to NO_2, which was suggested by reactions (2) and (3). These data were generated to illustrate the concept of the high temperature decomposition process and were not intended to provide the optimum conditions for the maximum degree of conversion, which is dependent on the application

EXAMPLE 2

For power plant applications the concentration of NO is typically in the 200–300 ppm range, which represents about 90 percent of the total NOx emissions with the remainder being primarily NO_2. Assuming that the total flow of the gas stream containing NO through the flue gas stack is 1,000,000 cfm, the amount of hydrogen peroxide can be calculated as follows:

at 300 ppm

NO concentration = 300 ppm in 1,000,000 scfm stack gas
Temperature after SOx scrubber 50° C.

wt. NO

300 cfm @ 50° C. = 254 scfm NO
254 scfm = 391 gm moles NO = 21.2 lbs of NO
$H_2O_2 + NO \rightarrow NO_2 + H_2O$

H_2O_2 required

1 mole NO reacts with 1 mole H_2O_2
Therefore: 21.2 lbs of NO required 24 lbs H_2O_2
or 48 lbs at 50 wt % H_2O_2 or 4.8 gal/min.

This example starts with a 50% hydrogen peroxide solution and passes it through a check valve to prevent back-flow. Then, the hydrogen peroxide solution is heated to raise the temperature to approximately 140° C. as illustrated in FIG. **1**. The heat vaporizes some of the water in the hydrogen peroxide solution and produces an enriched hydrogen peroxide solution and steam. The steam and the enriched hydrogen peroxide solution are impinged onto a heated (200–500° C.) surface. The heated surface in this example is covered by a catalytic coating of iron oxide because it produces a high degree of conversion. The resulting process causes the rapid decomposition of hydrogen peroxide to oxidative free radicals, hydroxyl and hydroperoxyl. These oxidative free radicals are produced in a flowing stream of NO where they rapidly oxidize it to NO_2.

Although the present invention has been disclosed in terms of a number of preferred embodiments, and variations thereon, it will be understood that numerous additional modifications and variations could be made thereto without departing from the scope of the invention as defined by the following claims.

What is claimed is:

1. A process for oxidizing nitric oxide comprising:

a) providing a stream of nitric oxide;

b) providing a surface heated to a temperature of 200–500° C. within said stream of nitric oxide;

c) providing a hydrogen peroxide solution,

d) impinging said hydrogen peroxide solution onto said heated surface, whereby said hydrogen peroxide solution is decomposed into a plurality of oxidative free radicals; and

e) further oxidizing said nitric oxide to form nitrogen dioxide using said plurality of oxidative free radicals.

2. The process of claim **1**, further comprising the step of heating said hydrogen peroxide solution before impinging said hydrogen peroxide solution onto said heated.

3. The process of claim **2**, wherein said hydrogen peroxide solution is heated to a temperature of 140° C. before impinging said hydrogen peroxide solution onto said heated surface.

4. The process of claim **1**, wherein said hydrogen peroxide solution contains 50 wt. % or less hydrogen peroxide.

5. The process of claim **1**, wherein said catalytic coating contains an oxide selected from the group consisting of silver oxide, iron oxide, ruthenium oxide, glass quartz Mo glass, Fe_3—xMn_xO_4 spinels, Fe_2O_3 with Cu ferrite, MgO and Al_2O_3.

6. The process of claim **1**, wherein said stream of nitric oxide contains 50–350 ppm nitric oxide.

7. The process of claim **1**, wherein said plurality of oxidative free radicals is selected from the group consisting of hydroxyl radicals and hydroperoxyl radicals.

8. A process for oxidizing nitric oxide comprising:

a) providing a stream of nitric oxide;

b) providing a heated surface within said stream of nitric oxide;

c) providing said heated surface with a catalytic coating containing an element selected from the group consisting of iron, chromium copper platinum, silver and palladium;

d) providing a hydrogen peroxide solution;

e) impinging said hydrogen peroxide solution onto said heated surface, whereby said hydrogen peroxide solution is decomposed into a plurality of oxidative free radicals; and

f) further oxidizing said nitric oxide to from nitrogen dioxide using said plurality of oxidative free radicals.

9. A process for oxidizing nitric oxide comprising:

a) providing a stream of nitric oxide;

b) providing a heated surface within said stream of nitric oxide;

c) providing a hydrogen peroxide solution;

d) heating said hydrogen peroxide solution to a temperature of 140° C.;

e) impinging said 140° C. hydrogen peroxide solution onto said heated surface, whereby said hydrogen peroxide solution is decomposed into a plurality of oxidative free radicals; and

f) further oxidizing said nitric oxide to form nitrogen dioxide using said plurality of oxidative free radicals.

10. A process for oxidizing nitric oxide comprising:

a) providing a stream of nitric oxide;

b) providing a surface heated to a temperature of 200–500° C. within said stream of nitric oxide;

c) providing said heated surface with a catalytic coating containing an element selected from the group consisting of iron, chromium, copper, platinum, silver and palladium;

d) providing a hydrogen peroxide solution;

e) impinging said hydrogen peroxide solution onto said heated surface, whereby said hydrogen peroxide solution is decomposed into a plurality of oxidative free radicals; and

f) further oxidizing said nitric oxide to form nitrogen dioxide using said plurality of oxidative free radicals.

11. A process for oxidizing nitric oxide comprising:

a) providing a stream of nitric oxide;

b) providing a heated surface within said stream of nitric oxide;

c) providing said heated surface with a catalytic coating containing an element selected from the group consisting of iron, chromium, copper, platinum, silver and palladium;

d) providing a hydrogen peroxide solution heated to a temperature 140° C.;

e) impinging said heated hydrogen peroxide solution onto said heated surface, whereby said hydrogen peroxide solution is decomposed into a plurality of oxidative free radicals; and

f) further oxidizing said nitric oxide to form nitrogen dioxide using said plurality of oxidative free radicals.

* * * * *